Dissertationes Forestales 36

Nitrous oxide emissions from selected natural and managed northern ecosystems

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Academic dissertation

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Nitrous oxide emissions from selected natural and managed northern ecosystems

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ABSTRACT

Microbial activity in soils is the main source of nitrous oxide (N_2O) to the atmosphere. Nitrous oxide is a strong greenhouse gas in the troposphere and participates in ozone destructive reactions in the stratosphere. The constant increase in the atmospheric concentration, as well as uncertainties in the known sources and sinks of N_2O underline the need to better understand the processes and pathways of N_2O in terrestrial ecosystems. This study aimed at quantifying N_2O emissions from soils in northern Europe and at investigating the processes and pathways of N_2O from agricultural and forest ecosystems. Emissions were measured in forest ecosystems, agricultural soils and a landfill, using the soil gradient, chamber and eddy covariance methods. Processes responsible for N_2O production, and the pathways of N_2O from the soil to the atmosphere, were studied in the laboratory and in the field. These ecosystems were chosen for their potential importance to the national and global budget of N_2O.

Laboratory experiments with boreal agricultural soils revealed that N_2O production increases drastically with soil moisture content, and that the contribution of the nitrification and denitrification processes to N_2O emissions depends on soil type. Laboratory study with beech (*Fagus sylvatica*) seedlings demonstrated that trees can serve as conduits for N_2O from the soil to the atmosphere. If this mechanism is important in forest ecosystems, the current emission estimates from forest soils may underestimate the total N_2O emissions from forest ecosystems. Further field and laboratory studies are needed to evaluate the importance of this mechanism in forest ecosystems. The emissions of N_2O from northern forest ecosystems and a municipal landfill were highly variable in time and space. The emissions of N_2O from boreal upland forest soil were among the smallest reported in the world. Despite the low emission rates, the soil gradient method revealed a clear seasonal variation in N_2O production. The organic topsoil was responsible for most of the N_2O production and consumption in this forest soil. Emissions from the municipal landfill were one to two orders of magnitude higher than those from agricultural soils, which are the most important source of N_2O to the atmosphere. Due to their small areal coverage, landfills only contribute minimally to national N_2O emissions in Finland. The eddy covariance technique was demonstrated to be useful for measuring ecosystem-scale emissions of N_2O in forest and landfill ecosystems. Overall, more measurements and integration between different measurement techniques are needed to capture the large variability in N_2O emissions from natural and managed northern ecosystems.

Keywords: Nitrous oxide, production and consumption processes, agricultural soils, municipal landfill, forest ecosystems, roles of soil and plants, flux measurement methods

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Helsinki, February 2007

Mari Pihlatie

LIST OF ARTICLES

This thesis is based on the following original articles. The papers are reproduced with the kind permission of the journals concerned.

I Pihlatie M., Syväsalo E., Simojoki A., Esala M. and Regina K. 2004. Contribution of nitrification and denitrification to N_2O production in peat, clay and loamy sand soils under different soil moisture conditions. Nutrient Cycling in Agroecosystems 70, 135-141.

II Pihlatie M., Pumpanen J., Rinne J., Ilvesniemi H., Simojoki A., Hari P. and Vesala T. 2006. Gas concentration driven fluxes of nitrous oxide and carbon dioxide in boreal forest soil. accepted in Tellus B

III Pihlatie M., Ambus P., Rinne J., Pilegaard K. and Vesala T. 2005. Plant-mediated nitrous oxide emissions from beech (*Fagus sylvatica*) leaves. New Phytologist 168, 93-98. doi: 10.1111/j.1469-8137.2005.01542x.

IV Pihlatie M., Rinne J., Ambus P., Pilegaard K., Dorsey J.R., Rannik Ü., Markkanen T., Launiainen S., and Vesala T. 2005. Nitrous oxide emissions from a beech forest floor measured by eddy covariance and soil enclosure techniques. Biogeosciences, 2(4), 377–387. SRef-ID: 1726-4189/bg/2005-2-377

V Rinne J., Pihlatie M., Lohila A., Thum T., Aurela M., Tuovinen J.-P., Laurila T. and Vesala T. 2005. Nitrous oxide emission from a municipal landfill. Environmental Science and Technology 39, 7790-7793.

AUTHOR'S CONTRIBUTION

I Pihlatie was responsible for setting up and conducting the measurements in the laboratory. She wrote the manuscript in co-operation with the other authors.

II Pihlatie took part with the other co-authors in the planning of the measurements. She was solely responsible for setting up and conducting the measurements, and analyzing the data from the chamber measurements and soil gas concentrations. The manuscript was prepared in co-operation with the other authors.

III Pihlatie took part with the other co-authors in planning the experiment. She was solely responsible for conducting the measurements and analyzing the data. The manuscript was prepared in co-operation with the other authors.

IV Pihlatie took part with the other co-authors in planning of the measurements. She conducted the eddy covariance measurements and soil sampling, and preparation. The manuscript was prepared in co-operation with the other authors.

V Pihlatie took part with the other co-authors in planning the experiment, and in setting up and conducting the eddy covariance measurements. The manuscript preparation was done in co-operation with the other authors.

TABLE OF CONTENTS

1 SUMMARY OF PAPERS

I In this paper we studied the N_2O production in agricultural peat, clay and loamy sand soils in laboratory conditions. The aim was to test whether the soils differ in N_2O production under different soil moisture conditions, and whether the contribution of nitrification to the total N_2O production differs from soil to soil. N_2O production was small in all the soils at dry to intermediate soil moistures (40 and 60% water-filled pore space, wfps). At 80% wfps the N_2O production increased in loamy sand soil, whereas the N_2O production in peat and clay soils remained low. At water saturation (100% wfps) N_2O production increased drastically in all the soils. Nitrification was the dominant N_2O-producing process in all dry to moist soils. In wet soils, nitrification dominated in sandy loam soil, while denitrification dominated in peat soil.

II In this paper we report N_2O and carbon dioxide (CO_2) fluxes in a Scots pine-dominated boreal forest soil measured by soil gradient and chamber methods. We also report seasonal variation in soil N_2O concentrations at different soil depths. The N_2O fluxes obtained by these two techniques varied from a small emission to a small uptake. The uppermost soil layer (O-horizon) was responsible for most of the N_2O production and consumption. The soil gradient and the chamber methods agreed well in the case of CO_2 fluxes, whereas with N_2O fluxes there was more variation between the two methods.

III The aim of this study was to test whether trees can transport N_2O from the soil to the atmosphere and hence contribute to the N_2O emissions from forest ecosystems. We used the foliage chamber method to measure N_2O emissions from the leaves of potted beech (*Fagus sylvatica*) seedlings. We measured the emissions after fertilizing the soil of the seedlings with ^{15}N-labelled ammonium nitrate ($^{15}NH_4{}^{15}NO_3$), and after exposing the roots to elevated concentrations of N_2O. In both experiments N_2O or N_2O + $^{15}N_2O$ produced in the soil was emitted from beech leaves into the atmosphere. Our experiments demonstrate the existence of a previously-overlooked pathway of N_2O emission in forest ecosystems, and stress the need for further investigations.

IV In this study we compared the eddy covariance (EC) and chamber methods to study N_2O emissions from a beech (*Fagus sylvatica* L.) forest in Denmark. The EC measurements were conducted below the forest canopy in the trunk-space and the emissions were compared with soil surface chamber measurements. The emissions of N_2O were small and close to the detection limit of the EC system. Partly as a consequence of this, the short-term temporal variability in N_2O fluxes measured by EC was high. The variability in the chamber measurements was much smaller and dominated by small-scale spatial variability. The highest emissions measured by the EC method occurred during the first week of May when the trees were leafing and the soil moisture content was at its highest. We demonstrate that the EC technique in the trunk-space is a promising tool to measure soil emissions of N_2O in forest ecosystems.

V In this paper we report the first measurements of N_2O emissions from a landfill by the eddy covariance (EC) method. The measurements were conducted during ten days at the municipal landfill of the Helsinki Metropolitan Area. In addition to the EC measurements, several chambers were used to study the spatial variability of the N_2O emissions, as well as to provide a comparison with the EC measurements. N_2O emissions in the landfill were highly variable and depended on the source area influencing the measurement. Overall, the emissions were about an order of magnitude higher than the highest emissions reported from Northern European agricultural soils, and two orders of magnitude higher than the

highest emissions reported from boreal forest soils. Due to the small area of landfills as compared to other land-use classes, the total N_2O emissions from landfills are of minor importance in considering the total emissions from Finland.

2 INTRODUCTION

Concern about the global climate change has increased the need for scientific knowledge on emissions of greenhouse gases from natural and managed ecosystems. Evidence is clear that the global climate is changing, and that human activities are greatly altering the atmospheric composition. The atmospheric concentrations of the main greenhouse gases carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) have increased markedly since the pre-industrial period. In 2005 the N_2O concentration in the atmosphere was approximately 319 ppb as compared to that of about 270 ppb during the pre-industrial period (IPCC 2007). Nitrous oxide has an atmospheric life-time of approximately 114 years, and its global warming potential with a 100-year period is 300 times stronger than that of CO_2 (IPCC 2001). Currently, N_2O is estimated to account for approximately 6% of the anticipated global warming (IPCC 2007).

Due to its long atmospheric life-time, part of the N_2O in the troposphere escapes into the stratosphere, where it takes part in ozone destructive reactions. Microbial activity in soils is the main source of N_2O to the atmosphere. In the IPCC 2001 report agricultural soils were estimated to be the main anthropogenic sources (4.2 Tg N yr^{-1}), while soils in tropical climate (3.0 Tg N yr^{-1}) and the oceans (3.0 Tg N yr^{-1}) were the main natural sources of N_2O (IPCC 2001, Mosier et al. 1998, Kroeze et al. 1999). The total emissions from natural sources (9.6 Tg N yr^{-1}) slightly exceeded the total emissions from anthropogenic sources (8.1 Tg N yr^{-1}) (IPCC 2001). Although N_2O emissions from terrestrial ecosystems have been relatively much studied during the last two decades, the uncertainties in the emission estimates are very large. Also, as the carbon (C) and nitrogen (N) cycles in ecosystems are strongly coupled, any change in the N cycling affects the C cycling, and hence indirectly adds uncertainties in the balances of other greenhouse gases.

The first studies on losses of N_2O from soils were already conducted in the 1950's. Arnold (1954) measured the evolution of N_2O from a wide range of soils under different moisture conditions. At that time he already suggested that N_2O was produced in dry soil via microbial oxidation of ammonium and in wet soils via microbial reduction of nitrate (Arnold 1954). Later, in the 1970's, atmospheric scientists found that N_2O released into the atmosphere through denitrification in soils and waters participated in the destruction of stratospheric ozone (Crutzen 1972, 1974). When in the 1980's N_2O was also found to act as a greenhouse gas, and hence contribute to the global climate change, extensive research activities were directed to identify and quantify the sources of N_2O to the atmosphere.

Very little data are available on N_2O emissions from northern ecosystems, especially from the boreal zone. The number of publications related to N_2O emissions from the boreal region is about one-third of the number of publications related to N_2O emissions from either temperate or tropical regions (www.isiknowledge.com). Climate in the boreal region is characterized by a long snow-covered winter and a warm summer. Variation in temperature and precipitation between the seasons and between years is large. Hence, the emission estimates or knowledge on N_2O-forming processes from warmer climatic regions cannot be directly applied to northern ecosystems.

The aim of this study was to analyze and quantify N_2O emission rates in selected northern terrestrial ecosystems, and to increase our understanding on the N_2O forming processes in these ecosystems. Particularly, the aim was to obtain information on N_2O emissions from ecosystems that have previously been very little studied and on mechanisms potentially important for the N_2O budget. More specific aims were:

- To assess the importance of the major N_2O forming processes to the N_2O emissions from boreal agricultural soils
- To quantify the N_2O emissions from boreal upland forest ecosystems and to examine the roles of different soil layers in the production or consumption of N_2O
- To examine whether trees can serve as conduits for N_2O from the soil to the atmosphere
- To quantify the N_2O emissions from municipal landfills, and to assess their contribution to the greenhouse gas budget of the landfills, and to the national N_2O budget
- To compare, test and develop flux measurement methods in order to obtain more reliable estimates of the N_2O fluxes in different terrestrial ecosystems

3 BACKGROUND

3.1 The terrestrial nitrogen cycle

In terrestrial ecosystems the majority of the nitrogen is bound to soil organic matter, vegetation and living organisms in the soil. Nitrogen is an essential nutrient and a constituent of amino acids and proteins in living organisms. Biological nitrogen fixation and atmospheric nitrogen deposition are the only natural process by which nitrogen can be brought into ecosystems. Many bacteria and algae, especially the symbiotic bacteria of the genus *Rhizobium*, are able to fix molecular nitrogen (N_2) from the atmosphere. Besides nitrogen fixation, decomposition of soil organic matter is a major source of mineral nitrogen to the plants and micro-organisms. The escape of nitrogen from the soil occurs via leaching of nitrate (NO_3^-) to waterways, or through gaseous losses as nitrogen oxides or molecular nitrogen (N_2) into the atmosphere. Even though gaseous losses of nitrogen into the atmosphere form only a minor part of the nitrogen cycling within the biosphere, these gaseous losses in the form of N_2O and NO are important to global climate change and to the photochemistry of the lower troposphere.

Nitrogen is generally a limiting resource in many terrestrial ecosystems, and hence any addition of nitrogen increases the growth of plants in these ecosystems. Agricultural ecosystems are extremes of high biomass productivity, requiring a high nitrogen input in the form of fertilizers. Natural ecosystems receive nitrogen only from the atmosphere and hence nitrogen is the limiting factor in the growth of plants.

The use of synthetic nitrogen fertilizers, and the emission of nitrogen oxides due to combustion processes have both altered the natural nitrogen cycling on the Earth. Nitrogen is mainly deposited as ammonium (NH_4^+) and nitrate (NO_3^-), that are substrates for N_2O-forming processes. Since pre-industrial times, the deposition of atmospheric nitrogen onto the forests of the Northern Hemisphere has increased from approximately 1 kg N to 5 kg N ha^{-1} yr^{-1} (Holland et al. 1999). Currently, the nitrogen deposition in many ecosystems in Central Europe exceeds the critical load of 10-20 kg N ha^{-1} yr^{-1} (Matson et al. 2002, Holland et al. 2005). Nitrate leaching and increased nitrogen oxide emissions from the soil are symptoms of the excess nitrogen in such ecosystems (Butterbach-Bahl et al. 2002, Matson et al. 2002, Holland et al. 2005). Due to the short atmospheric lifetime and hence limited long-range transport of most nitrogen-containing pollutants, the boreal forest region of Scandinavia receives markedly less nitrogen from the atmosphere than the more industrialized regions of Central Europe. It is uncertain whether or not the nitrogen deposition onto the boreal region will increase in the future; however, in a scenario with increased deposition, the nitrogen retention of these ecosystems may also be greatly changed.

3.2 Nitrous oxide emissions from northern terrestrial ecosystems

During recent years, information regarding N_2O emissions from northern ecosystems has markedly increased. Emissions of N_2O from soils in the boreal region vary from 0 to 25 kg N_2O-N ha^{-1} yr^{-1} (Martikainen et al. 1993, Nykänen et al. 1995, Kasimir-Klemedtsson et al. 1997, Regina et al. 1999, Maljanen et al. 2003, Regina et al. 2004). Most of the boreal

ecosystems studied are agricultural soils, and forested and natural peatlands. The highest N_2O emissions have been measured from agricultural peat soils (Kasimir-Klemedtsson et al. 1997, Regina et al. 2004) and afforested peat soils with former agricultural history (Maljanen et al. 2001, Mäkiranta et al. 2007). Due to the large nitrogen storage in the peat, N_2O emissions from afforested peatlands remain high even several decades after the forestation (Maljanen et al. 2001, Mäkiranta et al. 2007). The emissions from forested peatlands range from close to zero to several kilograms of nitrogen per hectare per year, and seem to depend on the nutrient status of the original peat (Martikainen et al. 1993, Nykänen et al. 1995, Regina et al. 1998, Alm et al. 1999, Klemedtsson et al. 2005). Due to their large areal coverage, forested peatlands are important sources of N_2O in Finland.

The smallest N_2O emissions in Finland have been measured in natural peatlands (Martikainen et al. 1993, Regina et al. 1999). Similarly to the drained forested peatlands, the emissions of N_2O from natural peatlands depend on the nutrient status of the peat. In natural peatlands, low N_2O emissions are often related to negligible amounts of nitrogen in the peat, and also to waterlogged conditions, in which the end-product of denitrification, if it takes place, is molecular nitrogen (N_2).

Scattered emission measurements or laboratory studies of N_2O production in northern upland forest soils indicate that these ecosystems are also very small sources of N_2O (Schiller and Hastie 1996, Paavolainen and Smolander 1998, Brumme et al. 2005). The studies on mineral upland forest soils, however, have been short and concentrated on investigating the effects of different forest management practices (Martikainen et al. 1993, Paavolainen et al. 2000, Maljanen et al. 2006). Very little data is available on the seasonal variation of N_2O emissions, for instance.

In northern soils, the production of N_2O does not cease during snow-covered winters. High N_2O emission peaks have been measured from agricultural soils in winter during freezing and thawing of the soil (Regina et al. 2004, Syväsalo et al. 2004, Koponen and Martikainen 2004, Koponen et al. 2004, Koponen et al. 2006). Winter-time N_2O emissions are estimated to make up 50 to 60% of the annual emissions from agricultural soils in Finland (Regina et al. 2004, Syväsalo et al. 2004).

3.3 Production and consumption of N_2O in terrestrial ecosystems

In the soil, N_2O can be formed in several coexisting processes that are regulated by the amount of different forms of nitrogen in the soil and the oxygen concentration (see Figs 1-2). The nitrification and denitrification processes dominate the N_2O production in soils and waters; however, N_2O can also be formed in the soil chemically via chemodenitrification. To help the reader to follow the discussion on the results and to show the complexity of N_2O formation, the major processes producing or consuming N_2O in terrestrial ecosystems, together with the factors regulating N_2O production, are explained in more detail below.

3.3.1 Autotrophic and heterotrophic nitrification

Nitrification is the oxidation of ammonium (NH_4^+) or ammonia (NH_3) (autotrophic nitrification), or organic N compounds (heterotrophic nitrification) to nitrite (NO_2^-) or nitrate (NO_3^-) (Groffman 1991, Bremner 1997, Wrage et al. 2001) (see Fig 1a). Bacteria of the genus *Nitrosomonas* carry out the oxidation of NH_4^+ to NO_2^- and those of the genus *Nitrobacter* oxidize NO_2^- to NO_3^-. The sequence of oxidation reactions of NH_4^+ or NH_3 to

NO_3^- is catalyzed by several enzymes (see Fig 1a). The oxidation of NH_4^+ to hydroxylamine (NH_2OH) is catalyzed by ammonia mono-oxygenase, the oxidation of NH_2OH to NO_2^- by hydroxylamine oxidoreductase, and the oxidation of NO_2^- to NO_3^- by nitrite oxidoreductase (McCarty 1999, Wrage et al. 2001). The availability of oxygen is essential, since each step of the oxidation reaction requires O_2. N_2O can be formed through the chemical decomposition of NH_2OH or NO_2^- (Wrage et al. 2001) or during the reduction of NO_2^- under anaerobic or microaerophilic conditions (Poth and Focht 1985).
Chemoautotrophic nitrifying bacteria gain energy from the oxidation of reduced nitrogen compounds to fix CO_2 to organic carbon (Simek 2000). Heterotrophic nitrification is identical to autotrophic nitrification with respect to the intermediates and products; however, instead of deriving energy from the oxidation process, heterotrophic nitrifiers use organic compounds as a source of carbon and energy. Also, the ammonium mono-oxygenase and the hydroxylamine oxidoreductase enzymes differ slightly between heterotrophs and autotrophs (Wrage et al. 2001), making it possible to identify the contribution of autotrophic and heterotrophic process to the nitrification.

Autotrophic nitrifying organisms are largely responsible for the nitrification in most soils. Heterotrophic nitrification may contribute significantly to nitrification in soil environments that contain more fungi than bacteria, such as acidic forest soils. This is because heterotrophic nitrification is considered to be more common among fungi than bacteria (Schimel et al. 1984, Papen et al. 1989, Anderson et al. 1993).

3.3.2 Denitrification

Denitrification is defined as the respiratory bacterial reduction of nitrate (NO_3^-) or nitrite (NO_2^-) to nitrogen oxides or molecular nitrogen (Knowles 1982, Bremner 1997, Einsle and Kroneck 2004) (see Fig 1b). N_2O is an obligatory intermediate of the reduction process catalyzed by the enzymes nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase (Einsle and Kroneck 2004) (see Fig 1b). Denitrifying micro-organisms are often facultative aerobic bacteria that are able to reduce nitrogen oxides when O_2 becomes limiting. Denitrifying micro-organisms derive energy mostly from organic substrates, and hence denitrification is mostly limited by the amount of readily-decomposable organic substrates in the soil.

3.3.3 Other N_2O-forming processes in soils

Nitrifier denitrification

Nitrifier denitrification is a pathway of nitrification followed by a reduction process that resembles denitrification (Wrage et al. 2001). The sequence of oxidation of NH_3 to NO_2^- and the reduction of NO_2^- to N_2O is carried out by autotrophic NH_3-oxidizers (Wrage et al. 2001). As the oxidation and reduction processes are considered to be essentially the same as in nitrification and denitrification, without the formation of NO_3^-, the enzymes that catalyze these steps are thought to be the same as for NH_4^+ oxidation and denitrification (Wrage et al. 2001) (see Fig 1).

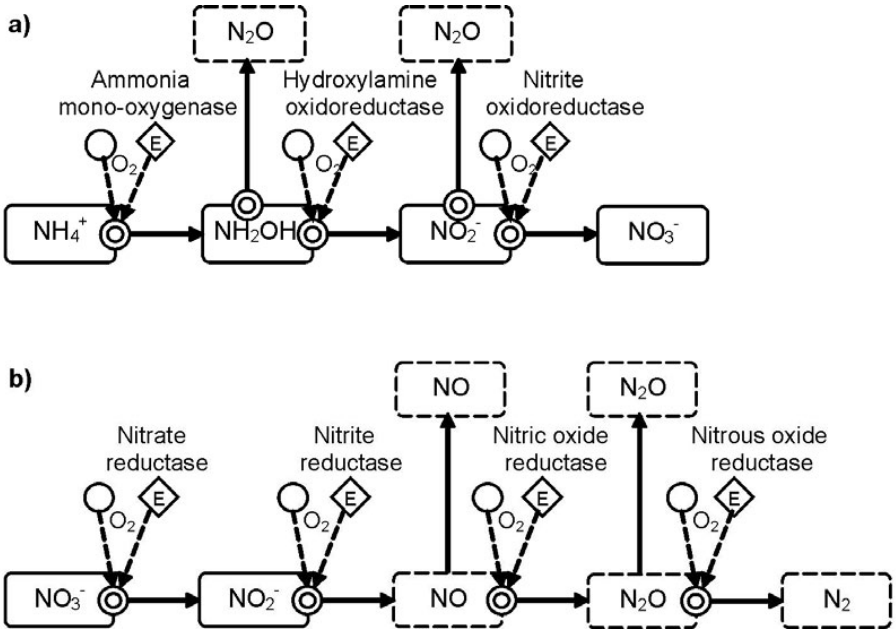

Figure 1. Autotrophic nitrification (a) and denitrification (b) pathways and enzymes involved in the processes (after Simojoki et al. 2007). Boxes denote concentrations of different nitrogen compounds in the soil, double circles represent biological or chemical processes, solid arrows show the flow of different forms of nitrogen in the soil and dashed arrows show the environmental factors (open circle) or enzymes (diamond) regulating the biological processes. The dashed line boxes denote gaseous forms of nitrogen.

Chemodenitrification

Small amounts of N_2O can be formed in the chemical decomposition of NO_2^- or other intermediates from the oxidation of NH_4^+ to NO_2^-. This process usually takes place at low pH, and the major product is NO, although some N_2O may also be produced (van Cleemput and Baert 1984, Bremner 1997).

Ammonia-oxidation by planctomycetes and Crenarchaeota

Recent findings on the ability of the microbial communities of planctomycetes and Crenarchaeota to oxidize ammonium reveal that the microbial nitrogen cycling in terrestrial ecosystems may be much more diverse than previously considered. The group of planctomycete-like bacteria oxidize ammonia with nitrite in strictly anoxic conditions in a process called anaerobic ammonium oxidation (anammox) (Strous and Jetten 2004, den Camp et al. 2006). The anammox bacteria are found in many marine and freshwater ecosystems; however, their contribution to ammonium oxidation in terrestrial ecosystems remains largely unknown. By contrast, crenarchaeota seem to be globally distributed and abundant in all major environments, including forest, agricultural, grassland and alpine soils, freshwaters and sediments (see Graeme and Schleper 2006). The suggestion of

Graeme and Schleper (2006) that the marine and terrestrial Crenarchaeota are major contributors to the biogeochemical transformations of nitrogen still remains to be elucidated.

3.3.4 Formation of N_2O in plant leaves

Nitrous oxide can be formed inside plant leaves during nitrate (NO_3^-) assimilation (Goshima et al. 1999, Smart and Bloom 2001). This non-respiratory non-bacterial reaction resembles microbial denitrification: N_2O is formed from NO_3^- and NO_2^- in a reaction catalyzed by nitrate reductase (NR) and nitrite reductase (NiR) enzymes (Dean and Harper 1986, Goshima et al. 1999, Smart and Bloom 2001). The capability of plants to convert NO_3^- or NO_2^- to N_2O seems common among different plant species, but the rate of N_2O formation is highly variable (Dean and Harper 1986, Goshima et al. 1999, Smart and Bloom 2001, Hakata et al. 2003). Hakata et al. (2003) estimated that the production of N_2O in plant leaves could account for up to 6% of the total N_2O emissions from agricultural plant-soil systems.

3.3.5 Coupling of the N_2O forming processes

Nitrification and denitrification in soils are often strongly coupled, and occur simultaneously in soils where the conditions favour both nitrification and denitrification. Nitrification in the aerobic microsites provides the substrates, NO_2^- and NO_3^-, for the denitrification that takes place in the anaerobic microsites. In a wet soil, the soil pore space is filled with water, and the diffusion of oxygen and other gases into the soil is slow. In locations of high microbial activity, oxygen may be readily used up and the conditions may change from aerobic to anaerobic.

Heterotrophic nitrifiers are able to denitrify under aerobic conditions where N_2O is produced as an intermediate in the reduction of NO_2^- to N_2 (Robertson and Kuenen 1991). This aerobic denitrification occurs when an organic substrate, oxygen and NO_3^- or NO_2^- are available (Robertson and Kuenen 1991). The quantification of the magnitude of this process is difficult, since the same heterotrophic nitrifiers are also able to nitrify in the presence of organic substrates. For this reason, aerobic denitrification and heterotrophic nitrification are often considered together.

Factors regulating autotrophic nitrification are the availability of carbon dioxide, oxygen and NH_4^+ -ions (Simek 2000). Carbon dioxide is very often present in soils, due to microbial and root respiration, whereas the concentration of molecular oxygen varies depending on the respiration activity and on soil aeration, which is affected by the balance between soil air filled porosity and soil moisture (Simek 2000, Simojoki 2001). In well-aerated soils, the availability of NH_4^+ is the limiting factor in autotrophic nitrification. In contrast to environments with an excess of nitrogen, environments a with very small soil nitrogen content often have low nitrification activity and as a consequence low N_2O emissions (Martikainen 1985, Priha et al. 1999, Priha and Smolander 1999). Factors regulating the rate of denitrification and the end-product formed in denitrification are the O_2 concentration, the availability of readily-decomposable organic matter, and the amount of NO_3^- and NO_2^- (Knowles 1982). The proportion of N_2O in the end product is higher if the soil pH is low, as the N_2O reductase is inhibited at low pH (Knowles 1982). In general, an increase in soil water content and temperature or the addition of fertilizer N, plant residues

or animal manures increase N_2O emissions from soils (e.g. Davidson 1991, 1993, Kaiser et al. 1998, Baggs et al. 2003, Schindlbacher et al. 2004).

3.4 Transport of N_2O from the soil into the atmosphere

3.4.1 Concentration-gradient-driven gas transfer

Molecular diffusion is the most important gas transport mechanism in the soil. Its effectiveness depends on the total porosity, the pore-size distribution and the amount and continuity of air-filled pores in the soil (e.g. Glinski and Stepniewski 1985, Simojoki 2001, Stepniewski et al. 2005). As the rate of diffusion in air for a given concentration gradient is 10 000 -fold compared with that in water, the amount of water strongly determines the rate of gaseous diffusion within the soil. Hence, if the transport characteristics and concentrations of gas in the soil, as well as soil moisture content, are known, the emission of gases from the soil to the atmosphere can be calculated. This approach was used in **paper II** to determine N_2O and CO_2 fluxes in a boreal Podzol forest soil.

Figure 2 gives a schematic presentation of the production, consumption and transport of N_2O in a Podzol soil profile. The soil horizons are typical for a boreal forest with a thin organic O-horizon and subsequent eluvial (A-) and illuvial (B-) horizons and parent material (C-horizon). Note that the soil-layer depths in Figure 2 do not represent the natural layer depths in a forest soil. In the soil, N_2O is microbially produced or consumed in the nitrification and denitrification processes. The production or consumption depends on the activity of soil microbes, which in turn depends on the availability of the substrates, NH_4^+ and NO_3^- ions, and organic carbon for the microbial processes. Soil temperature in general regulates the activity of soil microbes, while soil moisture regulates the aeration and gas diffusion in the soil. The transport of N_2O between the soil layers is driven by the concentration gradient. The physical structure of the soil and the proportion of air-filled pore space strongly influence the gas transport within the soil.

3.4.2 Plant-mediated gas transfer

Molecular diffusion is the main mechanism of gas transfer within plants (Armstrong, 1979). Plant species with an aerenchymatous structure are able to conduct gases from the root zone to the atmosphere (Rusch and Rennenberg 1998, Stephen et al. 1998). This phenomenon is well-documented for methane (CH_4) emissions from wetlands and rice paddies (Bubier 1995, Waddington et al. 1996, Stephen et al. 1998, Wassmann and Aulakh 2000, Strom et al. 2005). Plants can also serve as a conduit for dissolved gases from the root zone to the atmosphere (Chang et al. 1998, Yan et al. 2000, **Paper III**). Nitrous oxide as a water-soluble molecule can hence theoretically be taken up by the plant roots and transported to the leaves via the transpiration stream (Chang et al. 1998, Yan et al. 2000, Chen et al. 2002). This mechanism and its prevalence has, however, been very little studied, and estimates for the transpiration-driven plant-mediated N_2O emissions are based only on laboratory experiments.

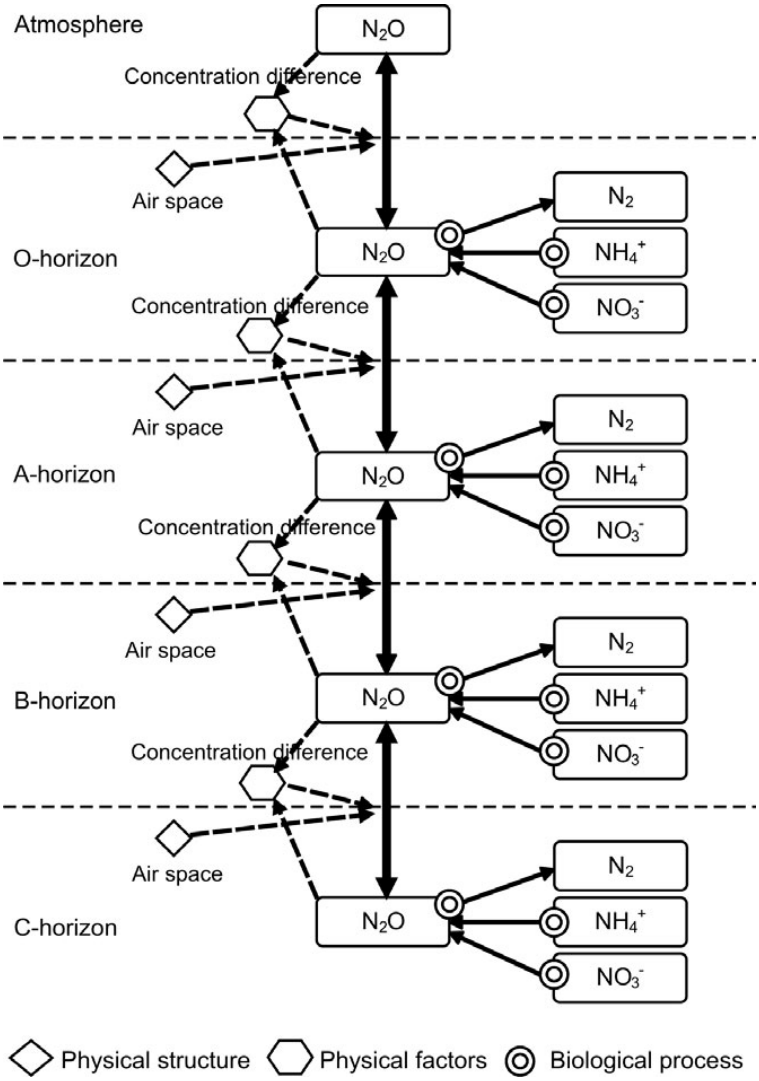

Figure 2. Production and transport of N_2O in the soil profile of a Podzol forest soil. Boxes denote the concentration of the various nitrogen compounds (N_2O, N_2, NH_4^+, NO_3^-) in different layers of the soil, bold arrows illustrate the transport of N_2O between the soil layers, thin arrows the flow of nitrogen (NH_4^+, NO_3^- or N_2O) in the soil and the dashed arrows the factors influencing the transport of N_2O between the soil layers.

Turbulent gas transfer

The part of the troposphere that is close to the Earth's surface is called the atmospheric boundary layer (ABL) (Stull 1988). As the ABL is directly influenced by the Earth's surface, the friction and heating of the surface induces vertical mixing of the air. This results in three dimensional swirling motions, also called turbulent eddies. Turbulent

transport is the most important vertical transport mechanism for trace gases, heat, water vapour and aerosol particles in the ABL (Stull 1988, Dabberdt et al. 1993).

Depending on the atmospheric stability, the height of the atmospheric boundary layer varies from tens of metres to several kilometres (Stull 1988, Dabberdt et al. 1993). During daytime, when the sun heats the surface, the ABL is at its deepest and is unstable and vigorously mixed. During night-time the surface cools down and the ABL becomes stable. This reduces turbulent mixing and the height of the ABL.

The region above the ABL is the free troposphere, where the effect of the earth's surface is not as evident. The lower part of the ABL is called the surface layer (SL) or the constant flux layer, which has a height of approximately 10% of the ABL height. In the SL the fluxes measured at an arbitrary height are equal to those at the surface (Dabberdt et al. 1993). Micrometeorological measurement techniques provide methods to analyze the characteristics of turbulence and to measure turbulent fluxes in the surface layer.

4 MATERIALS AND METHODS

This study is based on the measurements of N_2O emissions and of the factors regulating the emissions in different terrestrial ecosystems. The processes and pathways of N_2O from the soil to the atmosphere were studied in controlled laboratory conditions. In the field, N_2O emissions were measured in agricultural and forest ecosystems, as well as in a landfill, with several measurement techniques that differ from each other in their temporal or spatial scales (see Fig 1). The variables studied and the methods used in the different articles of this thesis are summarized in Table 1.

4.1 Measurement sites

Field measurements and soil samples for the laboratory experiments described in **paper I** were collected from three agricultural fields in Jokioinen, Southern Finland (60°49N, 23°30E) (see Fig 3). The experimental fields were established in 1999 on loamy sand, clay and peat soils, representing typical cultivated soils in Finland. The experiment was established to study greenhouse gas emissions from boreal agricultural soils during 1999-2002. The results of the field experiments regarding N_2O and CH_4 exchange have been published in Syväsalo et al. (2004) and Regina et al. (2004) and those of CO_2 exchange in Lohila et al. (2003).

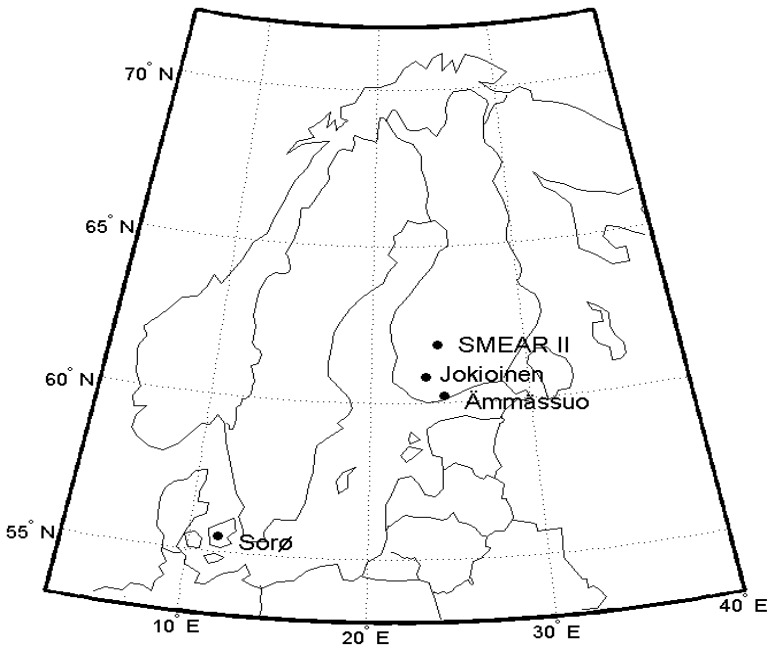

Figure 3. Location of the measurement sites Jokioinen (**paper I**), Smear II (**paper II**), Sorø (**papers III** and **IV**) and Ämmässuo (**paper V**).

Table 1. Variables studied and methods used in the various papers comprising the thesis.

Variable	Method	References	Paper				
			I	II	III	IV	V
Laboratory measurements							
Denitrification potential	Soil incubation with glucose + NO_3^-	Pell et al. 1998, Azam et al. 2002	x				
Nitrification potential	Soil incubation	Pell et al. 1998	x				
Leaf N_2O concentration	Equilibration of leaf material in glass vial with N_2O free air, gas chromatography	Paper III, Ambus et al. 2001				x	
Leaf fluxes of N_2O	Shoot enclosure technique, gas chromatography	Paper III, Ambus et al. 2001				x	
Leaf fluxes of $^{15}N_2O$	Shoot enclosure technique, mass spectrometry	Paper III, Ambus et al. 2001				x	
Leaf and air temperature	Testo thermohygrometer					x	
Chamber humidity	Raytek® infrared thermometer					x	
Chamber CO_2 concentration	IR Gas Analyzer, LI-COR					x	
Photosynthetically active radiation	LI-COR light meter and LI-COR Quantum Sensor					x	
Soil organic C content	Loss on ignition	Nelson and Sommers 1996	x		x		x
Soil total C	Dry combustion, IR spectrometry	Nelson and Sommers 1996	x				x
Soil total N	Dumas method	Bremner 1996	x				x
Soil mineral N content	Soil extraction with 1-2 M KCl, colorimetry	Mulvaney 1996			x		x
Soil bulk density	Volumetric soil sampling, core method	Blake and Hartge 1986a	x		x		x
Soil particle density	Pycnometer method	Blake and Hartge 1986b	x				
Soil pH (in H_2O or in $CaCl_2$)	Electrometric measurement	Thomas 1996	x		x		x
Soil porosity	Calculated from particle density and bulk density	Danielson and Sutherland 1986	x				x
	Table continues on the next page						

Variable	Method	References	Paper				
			I	II	III	IV	V
Field measurements							
Air temperature	Pt-100 sensors, shielded and ventilated	Haataja and Vesala 1997	x	x	x		x
Leaf area index	LAI 2000, plant canopy analyzer, LI-COR					x	
Litter collection	Litter collectors, collected fortnightly - monthly	Haataja and Vesala 1997					
Net N mineralization	Soil incubation in the field, ion spectrometry	Potila and Sarjala 2004					x
Precipitation	Raingauge, ARG-100	Haataja and Vesala 1997		x	x		x
Soil gas concentrations	Soil gradient technique, gas chromatography	Pumpanen et al. 2003					x
Soil fluxes of N_2O	Soil enclosure technique, gas chromatography	Regina et al. 2004	x	x	x		x
Soil fluxes of N_2O	Eddy covariance technique, TDL gas analyzer	Papers IV and V		x	x		
Soil moisture	Time domain reflectrometry, gravimetry	Haataja and Vesala 1997		x	x		x
Soil temperature	Thermistors, Philips KTY 80/110	Haataja and Vesala 1997	x	x	x		x

The measurements for **paper II** were conducted during 2002-2003 in Southern Finland at SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations) measurement station in a 40-year-old Scots pine (*Pinus sylvestris* L.) forest (61° 51'N, 24° 17'E) (Hari and Kulmala 2005) (see Figure 3). The site is located at Hyytiälä on a hill at 180 meters a.s.l.; the soil at the site is Haplic Podzol on glacial till (FAO-Unesco, 1990). Details of the measurements are given in **paper II**.

The field measurements described in **paper IV** were conducted in Denmark at Lille Bøgeskov (Small Beech-forest) near Sorø on the island of Zealand (55°29'N, 11°39'E) (see Figure 3). The measurements were conducted between 2 May and 5 June 2003. The forest is located in flat terrain and comprises about 1.5 square kilometres of mainly 82-year-old beech (*Fagus sylvatica* L.) trees. According to the American Soil Taxonomy system, the soil at the site is either Alfisol or Mollisol with a 10-40 cm deep organic layer. More details of the Sorø field site are given in Pilegaard et al. (2003) and in **paper IV**.

The beech seedlings for the laboratory experiment in **paper III** were collected from the same Lille Bøgeskov forest in 2001. The seedlings were potted and stored outside for 3 years until the laboratory experiment.

The field measurements of N_2O emissions from a municipal landfill, described in **paper V**, were conducted at the Ämmässuo landfill located in Southern Finland, 20 km northwest of the city of Helsinki (60°13'N, 24°36'E) (see Figure 3). The measurements were conducted during a 10-day period in August 2003. The landfill is operated by the Helsinki Metropolitan Area Council (YTV, http://www.ytv.fi/) and receives all the municipal waste from five municipalities with a total population of around one million.

4.2 Laboratory studies

4.2.1 Soil incubations

Paper I presents the results from an experiment to study the contribution of nitrification and denitrification to N_2O production in agricultural peat, clay and sandy soils. The soil samples were adjusted to four soil moisture contents: 40, 60, 80 and 100% of water filled pore space (wfps). The soil samples were incubated for five days in glass jars at room temperature. Gas samples were taken once a day from the headspace of the jars and analyzed for N_2O by a gas chromatograph. On the second day of incubation, acetylene (0.01%) was injected into the jar to block the nitrification activity in the soils and to investigate the contribution of nitrification to the total N_2O production. The daily N_2O production rates and the contribution of nitrification to the total N_2O production were estimated as explained in **paper I**.

4.2.2 Plant foliage enclosures

In **paper III** we studied whether beech (*Fagus sylvatica* L.) trees can act as conduits of N_2O to the atmosphere. More specifically, we conducted a laboratory experiment to test whether beech seedlings can transport N_2O from the soil solution to the atmosphere. We conducted two laboratory experiments. In the first experiment, the soil with the potted seedlings was watered with ^{15}N-labelled ammonium-nitrate-glucose solution. The seedlings were incubated over night and the emission of N_2O + $^{15}N_2O$ from the foliage was measured during two subsequent days.

In the second experiment, the soil around the beech seedlings was washed and the roots were inserted into a gas-tight pot with water and 1800 ppmv of N_2O in the headspace (Formánek and Ambus 2004, **Paper III**). To dissolve N_2O into the water the chamber was shaken carefully and allowed to equilibrate over night. The emission of N_2O from the foliage of the seedling was measured during the following days.

Leaf N_2O emissions were measured using a chamber enclosing only the foliage of a beech seedling. Air and beech leaf temperatures, relative humidity, photosynthetically active radiation and chamber air CO_2 concentration were monitored during the measurement. Pure CO_2 was injected to keep its concentration between 300 and 400 ppmv. Syringe gas samples were taken from the chamber air and analyzed for N_2O by a gas chromatograph equipped with an EC-detector and for $^{15}N_2O$ by a Finnigan MAT PreCon trace gas concentration unit combined with stable isotope ratio mass spectrometry.

4.2.3 Leaf N_2O concentration measurements

In order to estimate the possibility of leaf N_2O emissions in a forest, we analyzed the N_2O concentrations in the leaves of the laboratory seedlings and of beech trees in the Lille Bøgeskov forest (**paper III**). Leaves from the forest were sampled from tree branches at heights of 2 and 16 metres in the canopy. Fresh leaves were cut and inserted into glass vials, with a known leaf area per vial. The vials were flushed with nitrogen gas (N_2) to remove N_2O from the headspace. The vials were then equilibrated in the dark for several days to allow N_2O to diffuse from inside the leaf into the vial gas space. The concentration of N_2O inside the vials was analyzed with a gas chromatograph, while the concentration of N_2O inside the beech leaves was estimated. The concentration calculations are explained in detail in **paper III**.

4.3 Field measurement techniques

4.3.1 Soil-gradient method

In the soil-gradient method the concentrations of N_2O and CO_2 were monitored at different soil depths (**paper II**). The gas collectors, installed in the various soil layers, were sampled for soil air every fortnight or month and analyzed for N_2O and CO_2 by gas chromatography. The soil gradient method relies on a knowledge of soil structure, total porosity and soil water content, which are used as parameters in the flux calculation. The fluxes between the different soil layers were calculated using the model described in Pumpanen et al. (2003). The calculations are explained in detail in **paper II.** The concept of the model is shown in Figure 2.

4.3.2 Enclosure method

The enclosure technique was used in all the papers in this thesis. In this technique the soil or plant is covered with a box (chamber) with known dimensions and volume. The concentration of the target gas is monitored inside the chamber during the enclosure period. In the static chamber method, used in **papers I-V**, gas samples are taken at time intervals from the chamber air and the gas flux is calculated from the change in gas concentration during the enclosure period. In the dynamic chamber method, used for CO_2 in **paper II**, the

concentration of the target gas is continuously measured by drawing air from the chamber into an analyzer. To sustain a constant pressure inside the chamber, compensation air of a known gas concentration is led into the chamber. The flux is calculated from the mass balance of the gas concentration inside the chamber. The flux calculations for the chamber measurements are explained in more detail in **paper II**.

The static chamber measurements at each site were conducted using the same principle, the only differences being in the dimensions of the chambers and the enclosure time. At sites with high emission rates, e.g., agricultural fields and the landfill (**paper I** and **V**) the enclosure times were 10-30 minutes, whereas at the forest sites the enclosure times were up to 90 minutes (**paper II**). More details on the site-specific systems are given in **papers I-V**.

In **paper I** the chamber measurements were conducted to evaluate the contribution of nitrification to the N_2O production in the field. This was done by measuring the N_2O emissions from the chambers before and after treatment of the soil with a nitrification inhibitor, in our study, acetylene. For the nitrification inhibition, acetylene was injected into the headspace of closed chambers and left to affect for 18 hours. Thereafter the chamber lids were removed and the chambers vented for 24 hours, after which the emissions of N_2O were again measured.

4.3.3 Eddy covariance method

We used the eddy covariance (EC) technique in **papers IV** and **V** to study the N_2O fluxes in a forest and in a landfill. The micrometeorological EC technique relies on the measurement of the vertical wind velocity and the concentration of the target gas above the source or sink, for instance the soil surface. The measurements are conducted at a high time-resolution (~0.1 s) and the vertical flux of the target gas is calculated from the covariance of the vertical wind velocity and the gas concentration. The flux of the gas is given as an average over a specific time period, typically 30 minutes (Baldocchi 2003).

At both beech forest and landfill measurement sites in **papers IV** and **V**, the measurement system consisted of a tunable diode laser trace gas analyzer (TDL, TGA-100, Campbell Scientific Inc.) and a three-dimensional sonic anemometer (**paper IV**: Solent 1012, Gill Ltd., **paper V**: SWS-211, Applied Technologies Inc.). At both measurement sites the gas concentration and wind speed were measured at a height of 3 metres above the surface. In **paper IV** the EC measurements were conducted in the trunk-space of the beech forest, and in **paper V** on the open area of the municipal landfill.

5 RESULTS AND DISCUSSION

5.1 Emissions of N_2O from natural and managed northern ecosystems

Nitrous oxide emissions from all the measurement sites were characterized by high spatial variability (**papers II, IV** and **V**). In the field studies both this variability and the emission rates were highest at the municipal landfill and lowest in the boreal upland forest soil (**papers II**, **IV,** and **V**).

The emission of N_2O from the boreal Podzol forest soil varied from a small uptake to a small emission (**paper II**). The emissions over a one-year period averaged 0.35 μg N m^{-2} h^{-1}, which is of the same order of magnitude as the emissions from natural peatlands in Finland (Martikainen et al. 1993, Nykänen et al. 1995). Similar N_2O consumption rates as observed during spring-time in this Scots-pine-dominated Podzol forest soil in **paper II** have been reported in some nitrogen-limited temperate and Mediterranean forest ecosystems (Butterbach-Bahl et al. 1998, Goossens et al. 2001, Rosenkranz et al. 2006). Low N_2O emissions and an occasional consumption of N_2O have also been reported earlier from undisturbed and drained peatlands in Finland (Martikainen et al. 1993, Nykänen et al. 1995, Regina et al. 1999).

By extrapolating the N_2O emission rates from the upland forest ecosystem in this study to the whole area of upland forests in Finland, they are found to comprise approximately 4% of Finnish national N_2O emissions (Table 2). This equals the contribution of afforested peat soils that are considered as hot-spot sources of N_2O in Finland (Maljanen et al. 2003). Recently, Maljanen et al. (2006) reported N_2O emissions ranging from 11 to 17 μg N_2O-N m^{-2} h^{-1} from fertile spruce-dominated Podzol forest soil in southern Finland. The measurements in their studies were conducted in the summer and may hence be higher than the emissions in the winter. However, their findings indicate that boreal upland forest soils may be more important sources of N_2O than is estimated in this study.

Annual N_2O emissions from boreal agricultural soils range from 1.2 to 25 kg N ha^{-1} yr^{-1}, being one to two orders of magnitude lower than those from the municipal landfill in this study (see Table 2). N_2O emissions from agricultural peat soils are usually higher than those from agricultural mineral soils (Regina et al. 2004, Syväsalo et al. 2004). When the emissions from mineral and organic agricultural soils are multiplied by their respective areas, agricultural soils are seen to be the most important source of N_2O in Finland, accounting for approximately 60% of the total N_2O emissions from soils (Table 2).

The N_2O emissions from the municipal landfill in **paper V** are by far the highest emissions reported from soil ecosystems in Finland (Table 2). However, since the landfills cover a total of only approximately 1000 hectares of land area in Finland, their contribution to national N_2O emissions, 2%, is very small (Table 2). Despite their small contribution to national N_2O emissions, landfills are significant sources of other greenhouse gases, particularly, methane (IPCC, 2001, Laurila et al. 2005, Lohila et al. 2007).

Table 2. Emissions of N_2O from soils in Finland (mean, with range in brackets) and estimated contribution of different ecosystems to the N_2O budget in Finland.

Site	N_2O emission [kg N ha^{-1} yr^{-1}]	Source	Land area 1000 ha	Total N_2O emission [Gg N yr^{-1}]	% of the total emissions
Agricultural mineral soils	2.9 (1.2 – 7.8)	Syväsalo et al. 2004, Petersen et al. 2006, Syväsalo et al. 2006	2000	5.8	39.1
Agricultural organic soils	10.5 (4.0 - 25)	Nykänen, et al. 1995, Maljanen et al. 2003, Regina et al. 2004	300	3.2	21.1
Afforested peat soils	6.5 (1.0 - 30)	Mäkiranta et al. 2007	80	0.5	3.5
Forested peatland	1.0 (0.0 – 5.2)	Crill et al. 2000	5700	5.9	30.3
Undisturbed peatland	0.03 (0.0 – 0.09)	Crill et al. 2000	4000	0.1	0.8
Upland (mineral) forest soils	0.03	Paper II	17101	0.5	3.5
Landfills	230	Paper V	1	0.2	1.5
Total			29182	14.8	100

5.2 Factors regulating N_2O production and consumption in soils

Soil moisture is one of the key factors regulating N_2O production and its transport from soils (Schindlbacher et al. 2004, **Papers I, II** and **IV**). In **paper I** we investigated the effect of soil moisture on N_2O production in different agricultural soils under laboratory conditions. The greatest N_2O production occurred in water-saturated soils at 100% wfps (Figure 3). This was in line with field studies on N_2O emissions from agricultural soils (Dobbie et al. 1999, Simojoki and Jaakkola 2000, Dobbie and Smith 2001). In the field, large N_2O emissions have been related to denitrification, whereas in our laboratory experiment the dominating N_2O-forming process depended on soil type. Nitrification was the dominant N_2O-forming process in dry soils, whereas in water-saturated conditions denitrification dominated N_2O production in peat soil and nitrification in loamy sand soil. The results suggest that the response of N_2O production to soil moisture varies between different soils, and depend on soil structure, and the amount and availability of organic carbon and nitrogen in the soil.

Nitrous oxide production in the Podzol upland forest soil, presented in **paper II,** was clearly limited by the availability of mineral nitrogen. Several studies have shown that nitrification activities in boreal upland forest soils are very low (Martikainen 1984, Martikainen 1985, Paavolainen and Smolander 1998, Priha and Smolander 1999, Ambus et al. 2006). Despite this, the soil concentration measurements showed a clear seasonal variation in N_2O production in the organic topsoil of the Hyytiälä Podzol forest soil. The organic topsoil (O-horizon) was responsible for most of the N_2O production and consumption. The O-horizon acted as a source of N_2O in the autumn but as a sink of N_2O in the spring. In the autumn, it seems that a litter fall stimulated N_2O production in the topsoil. This may be explained by an increased organic matter mineralization in the litter and humus layer and a consequent release of mineral nitrogen into the soil. In nitrogen-limited soil, the newly-available mineral nitrogen may then be utilized by nitrifying and denitrifying bacteria to produce N_2O.

Since the processes responsible for N_2O consumption in soils are relatively little-studied, the environmental factors regulating the consumption of N_2O are not well known. Currently the only process known to consume N_2O is denitrification (Knowles 1982, Conrad 1996), whereas it has been hypothesized that heterotrophic nitrifiers could also reduce N_2O in aerobic conditions (Wrage et al. 2001, Rosenkranz et al. 2006). Both the low soil nitrogen content and high soil C content in the O-horizon of the upland forest soil in **paper II** favour anaerobic N_2O reduction by denitrifiers and aerobic N_2O reduction by heterotrophic nitrifiers (Wrage et al. 2001).

In **paper IV** we found that the N_2O emissions from a beech forest floor measured with the EC technique correlated positively with both soil water content and soil NH_4^+ concentration, but not with soil NO_3^- concentration (see Figure 4). The soil moisture in this study remained moderate, below 60% wfps throughout the measurement period. At such values of soil moisture content, nitrification and denitrification are considered to occur simultaneously and to both contribute to N_2O production (Davidson, 1991). The correlation with soil NH_4^+ concentration indicates that the N_2O production in this beech forest soil requires nitrification to take place. In a laboratory study, Ambus et al. (2006) found out that denitrification was mostly responsible for N_2O production in north European forest soils, including this beech forest in **paper IV**. Nitrification, however, had a key role in the control of N_2O production due to the supply of a substrate for denitrification.

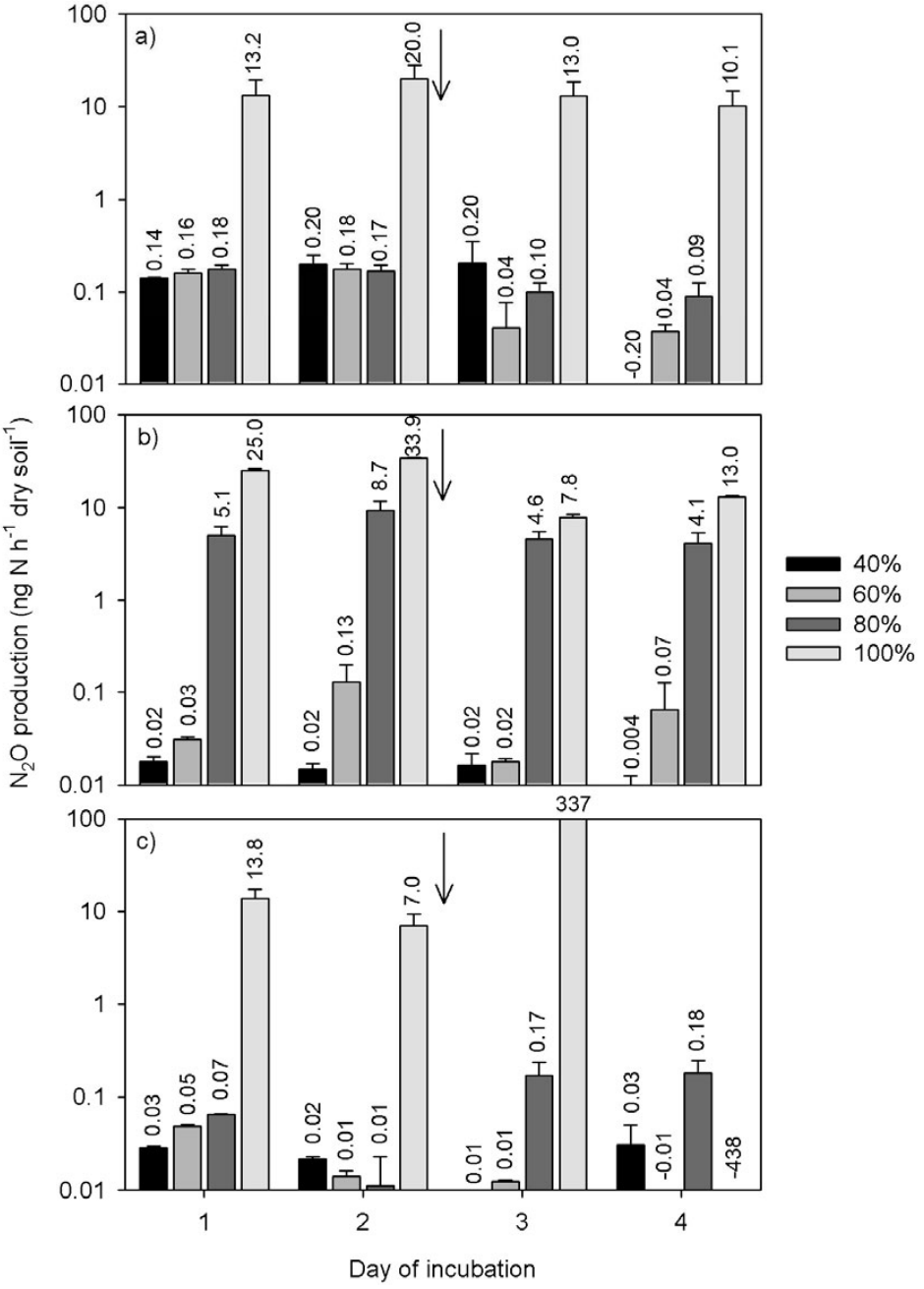

Figure 3. Nitrous oxide production rate in (a) peat, (b) loamy sand and (c) clay soils during four-day incubation in four different soil moisture conditions (40, 60, 80 and 100% water-filled pore space, wfps). The arrow indicates the timing of the acetylene addition to the incubation jars. Acetylene at low concentrations inhibits autotrophic nitrification, and hence can be used to evaluate the contribution of nitrification to the total N_2O production.

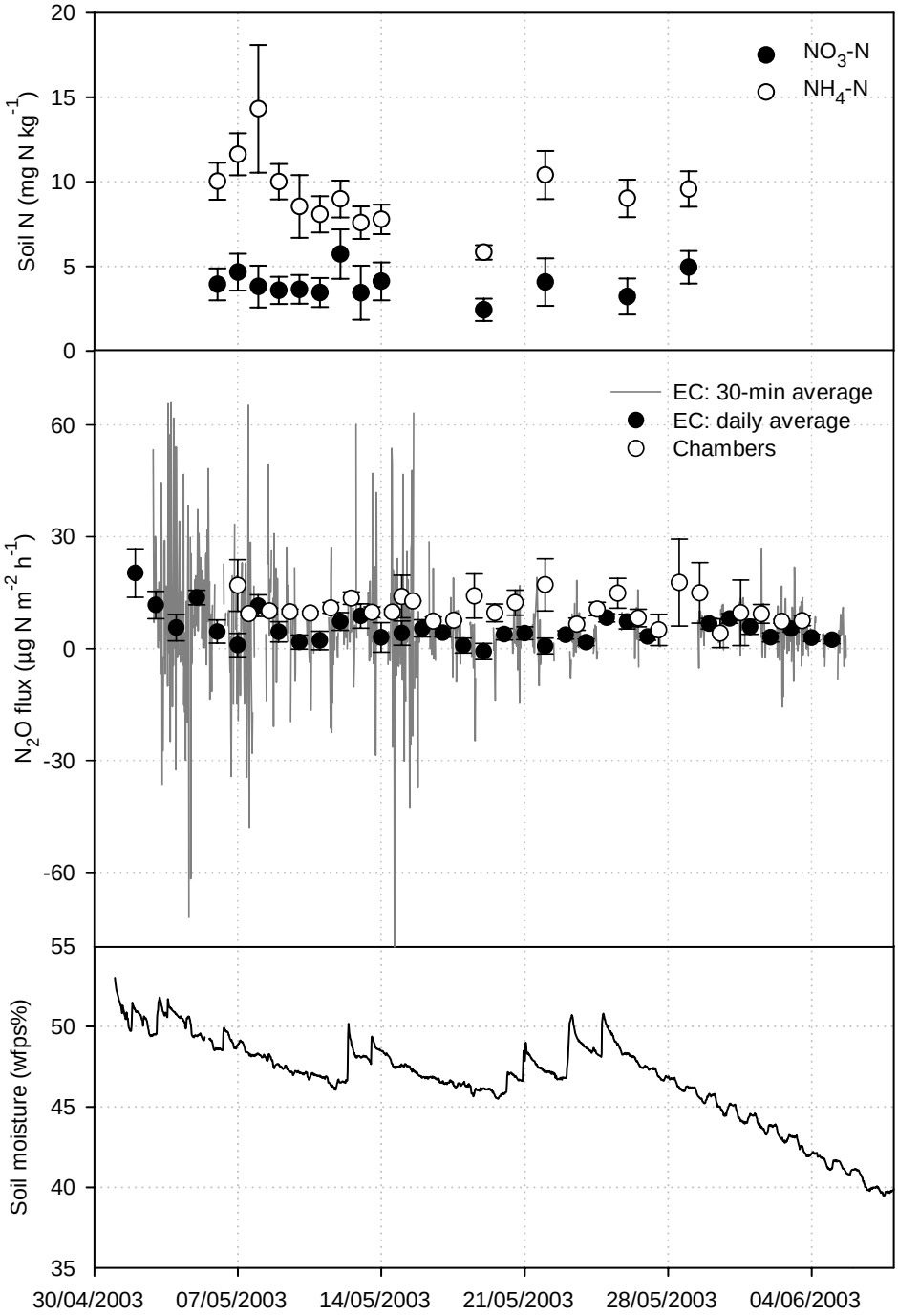

Figure 4. Soil mineral nitrogen content (top), N_2O fluxes measured with the eddy covariance (EC) and chamber techniques (centre), and soil moisture (bottom) in a beech forest in Denmark during a five-week measurement campaign. Data from **paper IV.**

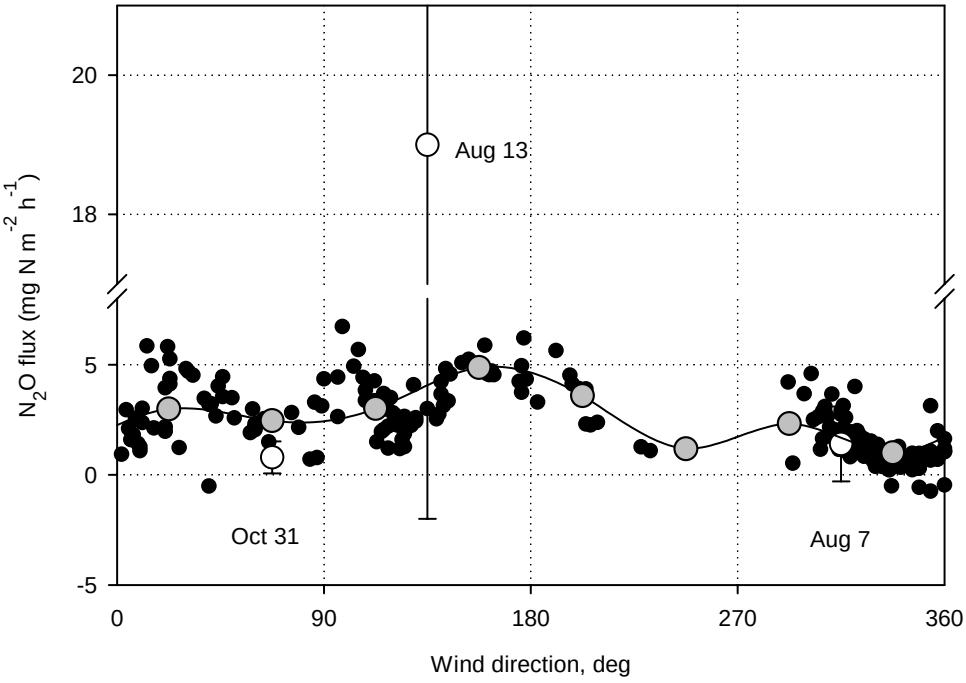

Figure 5. Nitrous oxide emissions as a function of wind direction during 8-18 August 2003 at the Ämmässuo landfill measured by eddy covariance (EC) and chamber techniques. The black circles represent half-hourly EC emissions, open circles the average emissions from soil chambers with 95% confidence intervals (10 chambers), while grey circles indicate EC N_2O emissions averaged over 45° wind sectors. Redrawn from **paper IV**.

In the beech forest floor and in the landfill (**papers IV** and **V**), where the N_2O emissions were measured continuously with both chamber and EC methods, no diurnal variability or correlation of N_2O emission with soil temperature was observed. This was in disagreement with the study of Maljanen et al. (2002), who found that N_2O emissions from boreal agricultural and forest soils follow the variation in top-soil temperature, particularly during seasons with a high variation in daily soil temperatures.

In the landfill, other factors than soil temperature and moisture regulated N_2O production. Higher N_2O emissions were measured from an area southeast than from an area west of the EC measurement tower (see Figure 5). This south-eastern area had a vegetation cover on the soil and contained older waste material than the area west from the EC tower (Figure 5). It can be speculated that in the older waste deposition area the soil micro-organisms had had a longer time to adapt to the environment, and the N_2O emission may have been the sum of different microbial processes taking place in the deep waste layers and in the cover soil (Bogner et al. 1999, Mandernack et al. 2000, **paper V**).

5.3 Contribution of trees to N_2O emissions from forest ecosystems

In **paper III** we discovered that beech (*Fagus sylvatica* L.) seedlings in the laboratory can transport N_2O from the soil solution to the atmosphere via the transpiration stream. Fertilization of the soil of the beech seedlings with ammonium-nitrate and glucose induced emissions of N_2O from the beech leaves. In the fertilization experiment, it was assumed that the soil fertilization stimulated N_2O production in the soil, and that this N_2O was taken up by the beech roots and transported to the leaves via the transpiration stream. As it was not possible to separate the origin of the N_2O in this experiment, the shoot emission was the sum of transpiration-mediated N_2O emissions and N_2O formation in the leaves (Smart and Bloom 2001, Hakata et al. 2003). In another experiment, N_2O was emitted from the beech leaves when the roots of the beech seedlings were exposed to an elevated concentration of N_2O in the soil solution. In this exposure experiment the solution in the root compartment was deionized water, which is depleted of NO_3^-. In this way we were able to eliminate any possible NO_3^- assimilation and consequent production of N_2O in the leaves. This experiment demonstrated that the N_2O emitted from the leaves originated from the root compartment and hence that a mechanism exists for transpiration-mediated transport of N_2O from the soil to the atmosphere.

Assuming a value of 5 for the leaf area index (LAI) of a broad-leafed forest ecosystem, the observed leaf-based N_2O emissions from the fertilization and the root chamber experiments correspond to area-based emissions of 5.2 and 10.0 μg N_2O-N m^{-2} h^{-1}, respectively. These rough estimates of the canopy emissions in a forest ecosystem are of the same order of magnitude as soil-derived N_2O emissions from North and Central European forest ecosystems (Butterbach-Bahl et al. 2002, Ambus et al. 2001, Beier et al. 2001). In the root chamber experiment, the beech seedlings were exposed to one to three orders of magnitude higher N_2O concentrations in the root solution than those measured in natural forest ecosystems (Heincke and Kaupenjohann 1999, Papen and Butterbach-Bahl 1999). Our results from the root chamber experiment thus more likely represent only a potential for transpiration-mediated N_2O emissions in forest ecosystems. The emission estimate from the ^{15}N fertilization experiment represents the situation in an N-affected forest ecosystem, and hence may apply to forests exposed to high atmospheric N-deposition or fertilization management, such as poplar plantations.

In order to evaluate the potential for N_2O emissions from forest canopies in a forest ecosystem, beech leaves were collected from the Lille Bøgeskov forest and analyzed for N_2O concentrations inside the leaves. The leaf N_2O concentrations in the forest trees were higher than the ambient atmospheric N_2O concentration, indicating that beech leaves may also be sources of N_2O in a forest. The leaf N_2O concentrations, however, were much smaller than those in the leaves of the laboratory seedlings, indicating that natural N_2O emissions are much smaller than those measured in the laboratory.

In order to estimate N_2O emissions from forest a canopy, the following exercise was done. The N_2O emissions from the forest canopy E_f were calculated as follows,

$$E_f = \frac{E_s}{c_s} c_f \qquad (1)$$

Where E_s is the N_2O emission from the laboratory seedlings [μg N_2O-N m^{-2} of leaves], c_s is the N_2O concentration inside the beech leaves of the laboratory seedlings, and c_f is the

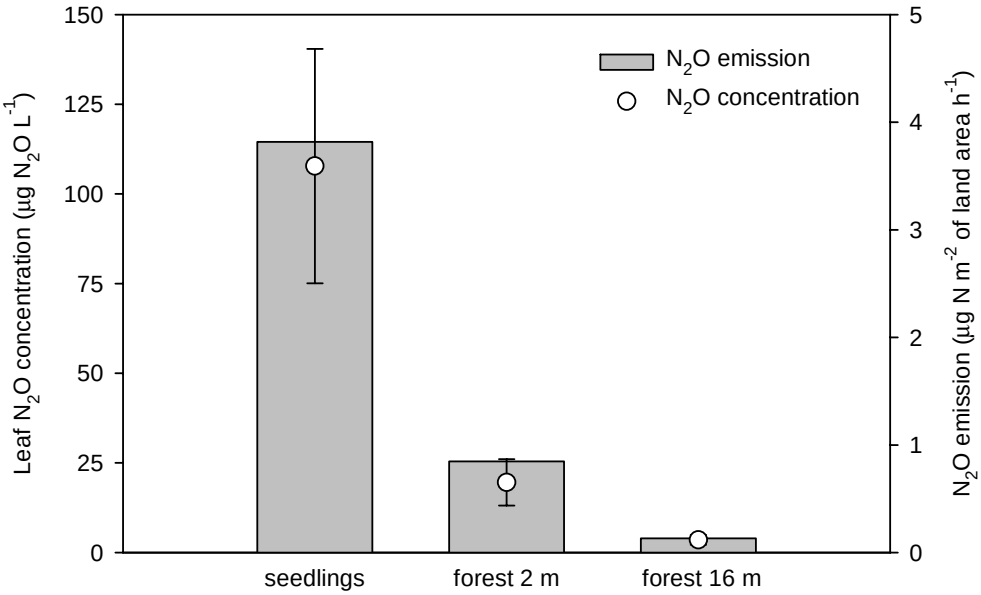

Figure 6. Concentration of N_2O inside beech (*Fagus sylvatica* L.) leaves of the laboratory seedlings and of tree branches collected from two heights (2 and 16 m) of the canopy in the Lille Bøgeskov forest. Emissions of N_2O from the leaves from the forest are calculated assuming the same concentration to emission ratio as that of the laboratory seedlings. The N_2O emissions from the forest canopy per land area are scaled up using leaf area indexes measured at 2 and 16 metres in the canopy.

N_2O concentration inside the beech leaves of the forest trees. This gives an emission estimate from the forest ecosystem as the N_2O emission per leaf area. The N_2O emissions at heights of 2 and 16 metres in the canopy corresponded to area-based emissions of 0.86 and 0.14 µg N_2O-N m^{-2} h^{-1}, respectively (Figure 6). These N_2O emission estimates from beech trees were much smaller than those of the laboratory seedlings, making up approximately 10% of the measured soil-emitted N_2O in this beech forest (Figure 6, **Paper III**). Despite the large uncertainties in these calculations, this exercise indicates that trees may significantly contribute to the N_2O emissions from forest ecosystems.

5.4 Discussion on methods for N_2O emission measurement

Paper II demonstrates that the soil gradient method has advantages over the chamber method in ecosystems with very small N_2O emission rates. As molecular diffusion is the only transport mechanism for the gases in the soil, the mixing of gases there is slow and the gases accumulate, assuming that the production of the target gas exceeds its consumption. Hence, the areas of N_2O production and N_2O consumption can be localized, and the fluxes between different soil layers can be calculated even from very small concentration differences. This is particularly good for soils with very low N_2O emissions such as the measurement site at Hyytiälä in **paper II**.

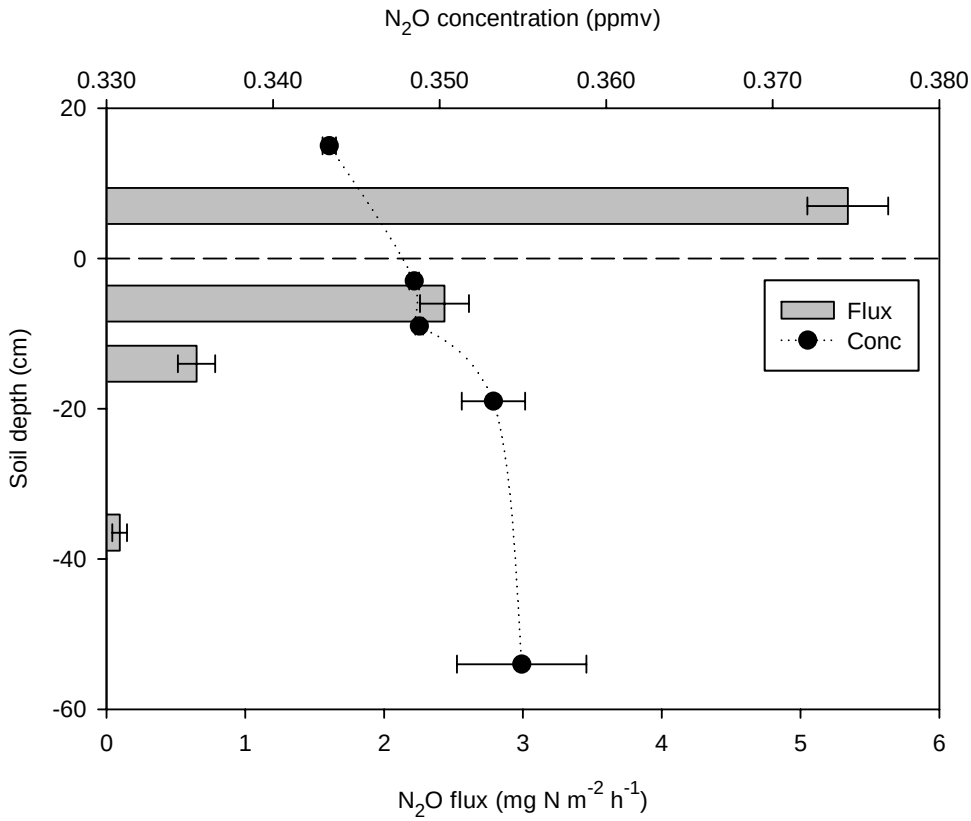

Figure 7. Measured N_2O concentrations and calculated N_2O fluxes from the soil profiles in boreal pine forest soil on 3 July 2003. The concentrations (black dots) represent mean values from four measurement locations; the fluxes are also mean fluxes from the four locations. **Paper II**.

In the Scots-pine-dominated upland forest soil, the chamber method was unable to capture the seasonal variation in the soil N_2O fluxes (**paper II**). The soil gradient method instead revealed a small but clear seasonal variation in the N_2O fluxes. It also showed that the top-most soil layer was responsible for most of the N_2O production and consumption in the soil. In both summer and autumn the uppermost soil layer (O-horizon) acted as a source of N_2O (Figure 7), whereas in the spring N_2O was consumed in the O-horizon. The disadvantages of the soil gradient method are the laborious installation of the gas collectors and soil sensors at different soil layers and the physical disturbance to the soil during the installation. Hence, the installation should be done carefully and well in advance of the start of the measurements.

The most common and often the most inexpensive field measurement method for N_2O emission measurements is the static chamber method (**papers I-V**). The chamber method provides the possibility of studying the small-scale (1 cm to 1 m) spatial variation of soil N_2O fluxes. It also makes it possible to link soil environmental parameters to N_2O production, assuming that the environmental parameters are measured in the vicinity of the chambers. One disadvantage of the chamber method is that the chamber frames physically

disturb the soil surface and may therefore influence the biological processes and gas transport (e.g. Gao and Yates 1998, Hutchinson et al. 2000, Conen and Smith 2000, Pumpanen et al. 2004, Livingston et al. 2005). Another problem discussed in **paper IV** and **V** is the number of chambers and frequency of sampling that are often insufficient to cover the spatial and temporal variability, respectively, in the N_2O emissions. In ecosystems with very large N_2O emissions and high spatial and temporal variability, the EC method may be more useful, as it integrates over soil locations having different N_2O production rates.

The static chambers used for N_2O emission measurements in the field have small differences with respect to design and operation. Discussions on ideal chamber designs are based on theoretical evaluations, and no tests of the performance of different chamber designs in controlled conditions exist. Such a chamber comparison, recently conducted for CO_2 flux chambers (Raich et al. 1990, Norman et al. 1997, Janssens et al. 2000, Pumpanen et al. 2004), would increase the reliability of the flux measurement and make it possible to compare fluxes measured at different sites.

The static chamber method has limitations in forest ecosystems, as tall trees do not fit inside closed chambers. Hence, evaluation of the contribution of forest trees to the N_2O emission from forest ecosystems is less straightforward to estimate than the contribution of plants in agricultural systems. The use of the EC method simultaneously below and above a forest canopy could be a potential method for estimating the contribution of trees to the total N_2O emission from forest ecosystems.

Papers IV and **V** demonstrate that the EC technique is a promising tool for studying N_2O fluxes on the ecosystem scale. It is especially suitable for environments with high emission rates, and a high spatial variability in emissions, such as landfills (**paper V)**. In **paper IV** we successfully used the EC technique in evaluating the spatial and temporal variability in N_2O emissions from a beech forest floor. Although the N_2O emissions were small and close to the detection limit of the measurement system, we were able to distinguish a definite day-to-day variation in the N_2O emissions, and link the N_2O emissions to soil water content and soil ammonium concentration (**paper IV,** Figure 4). A comparison of the mean fluxes from the chamber and EC methods showed good agreement between the two methods. The fluxes measured by these two techniques were of the same order of magnitude, but the variation in the fluxes measured by the EC method was much higher than that measured by the chambers (see Figure 4). A large part of this high variation resulted from instrumental random errors when measuring fluxes close to the detection limit. Part may have resulted from a real temporal and spatial variation in the N_2O fluxes, or in emissions from the leaves of the forest trees not captured with the soil chambers (**paper IV**). In the landfill the variability in N_2O emissions was so high that the ten chambers used were still insufficient to cover the spatial variability (**paper IV** and Figure 5). Particularly on August 13 one of the chambers was clearly on a hot-spot location with an N_2O emission that was an order of magnitude higher than the other chambers. The EC method has clear advantages over chamber methods in environments where the surface of the soil is so heterogeneous that the placement of soil chambers is difficult, or during seasons when snow-cover or freezing and thawing of the soil prohibits chamber measurements (Rinne et al. 2006).

The EC method, like any other method, also has its limitations. First of all, it requires a large homogenous and flat source area (Baldocchi 2003). Further challenges arise when measuring fluxes close to the detection limit of the measurement system as the EC method usually has a higher detection limit than the chamber method.

5.5 Future considerations

In this work the aim was to quantify the N_2O emission rates from forest soils, and a landfill. Currently, the emission estimates from boreal agricultural soils are based on chamber measurements conducted once a week or once a month. Such a measurement frequency misses the possible short-term variation or pulses in N_2O emissions, and may lead to under- or overestimation of the emission rates. The EC method would be a good tool to study the temporal variation in N_2O emissions related to, for instance, freezing-thawing events or the application of fertilizers to agricultural soils. The use of the EC method would be particularly useful during periods when chamber measurements are difficult to conduct, such as in winter.

The fact that boreal forests cover 59% of the land area in Finland (Finnish Statistical Yearbook of Forestry 2005) and 11% of the land area of the whole world (Archibold 1995) increases the importance of accurate estimations of N_2O emissions from these ecosystems. The current emission measurements from boreal upland forest soils are scattered and mainly concentrated on summer-time periods. To my knowledge, **paper II** represents the only annual measurements so far conducted on upland boreal forest soils in Finland. Clearly more year-round measurements of N_2O emissions from boreal forest soils are needed to evaluate the importance of winter-time emissions to the annual N_2O budget. If the winter-time N_2O emissions from boreal forest soils turn out to be as important as the winter-time N_2O emissions from agricultural soils, the annual N_2O emissions cannot be estimated without winter-time measurement data.

One clear uncertainty in N_2O emission estimates from forest ecosystems is the contribution of trees to the total N_2O emission. The laboratory results of the N_2O transport from the soil to the atmosphere via the transpiration stream raises the need for further research both in the laboratory and in the field. Since all the current N_2O emission estimates from forest ecosystems are based on emission measurements from the soil by chambers, the potential additional emission of N_2O from the forest canopies should be accounted for.

An overall aim in the future should be to lower the uncertainties in N_2O emission estimates from different ecosystems and to obtain more information on the processes producing and consuming N_2O in terrestrial ecosystems. Effort should be put into linking the field and laboratory measurements to the modelling of N_2O emissions from different ecosystems.

6 SUMMARY AND CONCLUSIONS

Nitrous oxide emissions from agricultural soils, which are the main source of N_2O in Finland, increase drastically with increasing soil water content. Most of the N_2O production in clay, sandy and peat soils close to field capacity, originated from microbial nitrification. Denitrification was the dominant N_2O-forming process only in wet peat soil. This information on the contribution of nitrification and denitrification to the total N_2O emissions in different agricultural soils is valuable for process-based modelling of N_2O emissions from soils with different textures.

According to this study, the N_2O emissions from northern terrestrial ecosystems vary greatly both in space and in time. The emission rates increased in the order of boreal Scots-pine-dominated forest soil < temperate beech forest soil < boreal agricultural soils < municipal landfill. N_2O emissions from Podzolic upland forest soils are very small, contributing approximately 4% of the N_2O emissions from soils in Finland. Despite the small emissions from Podzol upland forest soil, a clear seasonal variation in N_2O production was observed. Nitrous oxide was produced in the organic topsoil during summer and autumn, and consumed in the same layer in the spring. In the future, the projected increase in temperature and a possible increase in nitrogen deposition onto boreal forests may alter nitrogen cycling and consequent N_2O production. The potential changes in the nitrogen cycling stress the importance of long-term monitoring of emissions from boreal ecosystems.

In this study we found that trees can serve as conduits of N_2O from the soil to the atmosphere. This pathway for N_2O from soils to the atmosphere has previously been overlooked in the emission inventories. The magnitude of the tree-mediated N_2O emissions from forest ecosystems should be investigated on larger scales. Overall, accounting for this phenomenon may change the N_2O emission estimates from forest ecosystems.

Nitrous oxide emissions from a municipal landfill per unit land area were found to be one to two orders of magnitude higher than that from agricultural soils, and up to three orders of magnitude higher than the emissions from forest soils. However, due to their small areal coverage, the contribution of landfills to the total N_2O emissions in Finland is minimal, less than 2%.

The soil gradient method was found to be a useful measurement technique in environments with very small N_2O emissions, such as the Podzolic upland forest soil in this study. The chamber method, as the most common flux measurement method, gives valuable information on the small-scale variation in N_2O emissions. However, if the chamber method is used to estimate emission rates on the ecosystem scale, the number and the placement of chambers becomes important in order to sufficiently cover the spatial variability in soil N_2O emissions. The micrometeorological EC technique was found useful in studying the spatial and temporal variability in N_2O emissions in a landfill and in a forest ecosystem. The EC technique was found particularly useful in ecosystems with high N_2O emissions, such as landfills.

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